30

Curing Skins With Salt Containing Sodium Carbonate or Sodium Sulfate

By L. S. STUART *Associate Bacteriologist*, and R. W. FREY, *Chief, Hides, Tanning Materials, and Leather Division, Eastern Regional Research Laboratory, Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture.*

The controlling influence of moisture on the microbial deterioration of salt-cured hides and skins has been definitely established.[1,2] Thus, it is obvious that any impurities in the salt used for curing or any materials added to it that affect materially the hygroscopic properties of cured hides or skins may exert through this property alone marked influences on microbial activity.

The hygroscopic properties of sodium chloride can be modified appreciably by mixing with it less than 1 per cent of certain salts. This fact provided the basis for the development by manufacturers of table salt of the free flowing or "pouring" variety in which a fraction of 1 per cent of magnesium carbonate is incorporated.

Recently Innes[3] compared the hygroscopic properties of sodium sulfate and sodium chloride and pointed out that skins cured with sodium sulfate were less hygroscopic than those cured with salt and, therefore, could be stored and shipped in humid tropical climates with a greater degree of safety.

The work to be described was undertaken to determine the influence of sodium carbonate and sodium sulfate on the hygroscopic properties of cured calfskin when used in the curing salt to the extent of 1 per cent, respectively, on the weight of the salt and further, to ascertain if this influence was great enough to bring about a better preservation.

Thirty-six samples, each 4 inches square, were cut from the bend portion of a freshly flayed, clipped, 9-pound calfskin. These were divided into three groups of 12 samples each and salted on the flesh side with one-third of their weight of untreated or treated salt as follows:

Group 1: salted with pure C.P. sodium chloride.
Group 2: salted with pure C.P. sodium chloride, plus 1 per cent anhydrous sodium carbonate.
Group 3: salted with pure C.P. sodium chloride, plus 1 per cent anhydrous sodium sulfate.

Immediately after salting, the pieces in each group were piled one on the other, flesh side up, and stored in separate, closed, humid chambers on a flat glass platform to allow the salt soluble proteins to drain away completely. After two weeks of curing in this manner the pieces were taken from the humid chambers and excess salt removed from them. The first, fourth, eighth, and twelfth pieces of each pile were diced into particles about

one-quarter inch square. These were thoroughly mixed to represent composite samples for each group and were used for the determination of moisture and salt. Moisture was determined by drying in an oven at 60° C. for 48 hours. The salt content was calculated from total chlorides determined by digestion of portions of the dried samples in concentrated nitric acid in the presence of an excess of standard silver nitrate solution followed by titration with 0.1*N* sodium sulfocyanate in the presence of a ferric indicator. From the results of these determinations the following moisture and salt contents were obtained for the cured skins in each group:

Group 1: moisture, 46.7 per cent; salt, 13.3 per cent.
Group 2: moisture, 47.0 per cent; salt, 13.1 per cent.
Group 3: moisture, 47.2 per cent; salt, 13.0 per cent.

The remaining eight pieces in each group were placed, flesh side up, in individual tared culture dishes and weighed. Each culture dish was then immediately put inside an individual glass chamber over a humidifying solution. For humidifying, sulfuric acid solutions made up according to Wilson[4] to give relative humidities of 100, 96, 92 and 88 per cent, respec-

TABLE I

Moisture Content of Cured Calfskin Pieces Stored at Different Relative Humidities for Intervals of Time up to 42 Days at 30° C.

Relative Humidity at 30° C.	Cured with	Initial Moisture Content	Moisture Content After Incubation at 30° C. for: 5 Days	10 Days	20 Days	30 Days	42 Days
Per cent		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
100	Salt alone	46.7	56.4	61.2	65.1	70.3	72.8
	Salt + 1 per cent anhydrous Na_2CO_3	47.0	56.0	61.2	64.7	71.1	73.6
	Salt + 1 per cent anhydrous Na_2SO_4	47.2	56.2	60.9	65.0	70.8	72.1
96	Salt alone	46.7	50.8	54.7	59.1	63.1	69.1
	Salt + 1 per cent anhydrous Na_2CO_3	47.0	50.3	52.4	53.2	53.7	54.8
	Salt + 1 per cent anhydrous Na_2SO_4	47.2	55.7	56.4	56.3	56.7	56.8
92	Salt alone	46.7	47.4	47.8	48.0	48.9	51.3
	Salt + 1 per cent anhydrous Na_2CO_3	47.0	46.9	46.6	45.3	44.0	42.4
	Salt + 1 per cent anhydrous Na_2SO_4	47.2	45.6	44.5	44.4	43.9	42.2
88	Salt alone	46.7	45.9	43.9	37.3	35.7	32.5
	Salt + 1 per cent anhydrous Na_2CO_3	47.0	45.3	44.2	40.1	36.3	33.0
	Salt + 1 per cent anhydrous Na_2SO_4	47.2	45.6	45.4	41.3	37.8	32.2

tively, were employed. Duplicate chambers were used at each humidity for the pieces of skin from each group. All chambers were incubated at 30° C. for 42 days. During the incubation period the humidifying solutions were adjusted weekly. Even so, some changes in their concentration no doubt occurred because of the loose-fitting covers of the humid chambers and the periodic opening of the chambers for weighing the pieces. The results, therefore, should be considered only as of comparative value. All pieces were weighed after 5, 10, 20, 30, and 42 days incubation. Changes in the moisture content of the pieces as calculated from these weights are given in Table I, without correction for those cases in which small quantities of liquor collected in the bottom of the culture dish.

The figures in Table I show that all the cured pieces of skin when stored in a saturated humidity absorbed water rapidly. Within five days the moisture content of all pieces had increased to well above 50 per cent and with continued incubation they took up moisture at almost an identical rate with eventual accumulation near the end of 42 days of a small quantity of liquor in the culture dish.

When stored at 96 per cent relative humidity the pieces of skin cured with salt alone behaved similarly to those stored at 100 per cent relative humidity, except that the moisture uptake was not quite so rapid or great. The pieces of skin that had been cured with salt plus 1 per cent of anhydrous

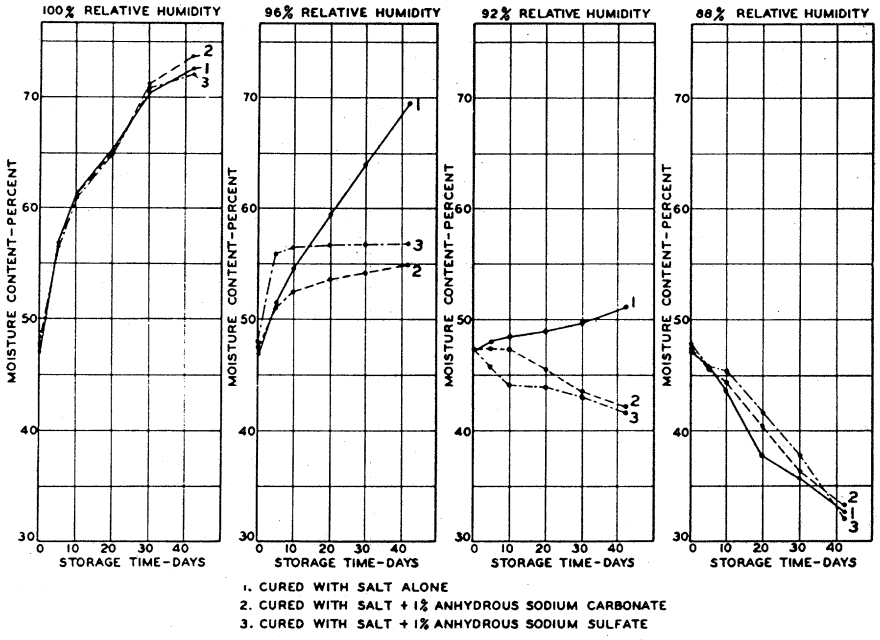

FIGURE I. Moisture content of cured calfskin stored at 30° C. and different relative humidities for intervals of time up to 42 days.

sodium sulfate took up water very rapidly during the first 5 days. From then on, however, the absorption slowed down materially and the moisture content did not exceed 56.8 per cent at the end of 42 days. No liquor accumulated in the culture dish. With those pieces cured with salt plus 1 per cent anhydrous sodium carbonate the rate of moisture uptake was much slower than with the others and the final moisture concentration was only 54.8 per cent after 42 days' storage.

When stored at 92 per cent relative humidity, those pieces cured with salt alone absorbed moisture at a slow but relatively constant rate, the final moisture content being 51.3 per cent after 42 days. In contrast to this there was a steady decrease in moisture content when either sodium sulfate or sodium carbonate was mixed with the salt, the amount of moisture present in the skins being 42.2 and 42.4 per cent, respectively, after 42 days.

At 88 per cent relative humidity all the pieces showed a comparatively rapid rate of drying out with a final moisture content ranging from 32.2 to 33 per cent.

The data given in Table I may be more readily visualized from the graphic presentation in Figure I.

TABLE II

Total Soluble Nitrogen, Ammonia Nitrogen, and Bacterial Count for Cured Calfskin Samples Stored at 30° C. and Different Relative Humidities for 42 Days.

Relative Humidity	Cured Previous to Storage for 14 Days with:	Total Soluble Nitrogen[1]	Ammonia Nitrogen[1]	Bacterial Count[1]
Per cent		Equiv. mls. 0.1*N* HCl	Equiv. mls. 0.1*N* HCl	Millions
100	Salt alone	1.333	0.866	6,027
	Salt + 1 per cent anhydrous Na_2CO_3	1.147	0.794	4,562
	Salt + 1 per cent anhydrous Na_2SO_4	1.138	0.718	5,768
96	Salt alone	0.701	0.389	5,109
	Salt + 1 per cent anhydrous Na_2CO_3	0.329	0.223	689
	Salt + 1 per cent anhydrous Na_2SO_4	0.436	0.231	861
92	Salt alone	0.389	0.282	603
	Salt + 1 per cent anhydrous Na_2CO_3	0.344	0.145	256
	Salt + 1 per cent anhydrous Na_2SO_4	0.300	0.192	288
88	Salt alone	0.300	0.171	287
	Salt + 1 per cent anhydrous Na_2CO_3	0.347	0.145	258
	Salt + 1 per cent anhydrous Na_2SO_4	0.283	0.136	315

[1]Per gram of original green salted skin.

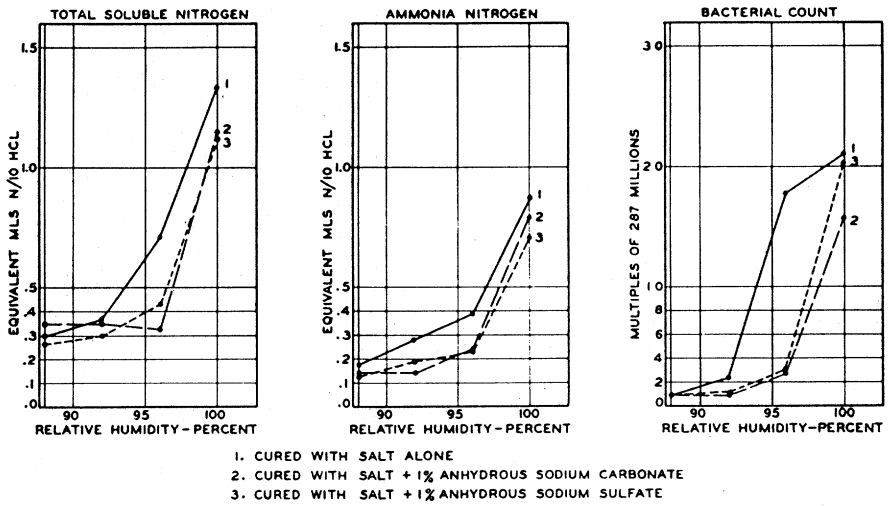

FIGURE II. Total soluble nitrogen, ammonia nitrogen, and bacterial count for cured calfskin stored at 30° C. and different relative humidities for 42 days.

At the conclusion of the 42-day incubation or storage period each sample was soaked for four hours in a volume of water equal to six times the weight of the sample. The soak-water, drainings, and washings from each culture dish were then combined and brought to a volume of one liter. Aliquots were removed for the determination of total soluble nitrogen, ammonia nitrogen, and bacterial count.

Total soluble nitrogen was determined by the K.G.A. method. Ammonia nitrogen was determined by magnesium oxide distillation. The bacterial counts were made by a modification of Breed's direct microscopic method as described in a previous publication[1]. The results are expressed on the basis of 1 gram of the original salt-cured skin and are given in Table II. They are averages of duplicate determinations.

From Table II it will be seen that microbial activity, as reflected by the nitrogen figures and bacterial count, decreases steadily with a lowering of the relative humidity at which the skins were held. In a saturated atmosphere at 100 per cent relative humidity all the pieces of skin had a moisture content of well over 50 per cent during the entire storage period and under this condition they all showed essentially the same results for nitrogen and bacterial count, regardless of whether cured with salt alone or salt mixed with either sodium carbonate or sulfate. Differences, however, begin to show up for storage at 96 per cent relative humidity. At this condition the pieces cured with salt alone had an appreciably higher moisture content than those cured with salt plus the carbonate or sulfate. At 92 per cent relative humidity the moisture content of the pieces did not exceed 50 per cent except in the single case where salt alone was used and the pieces

stored for 42 days. There is for this condition a definite trend toward lower and agreeing results for all three cures and this trend is practically attained at 88 per cent relative humidity. At this last condition all pieces of cured skin continued to lose moisture during storage and at no time had a moisture

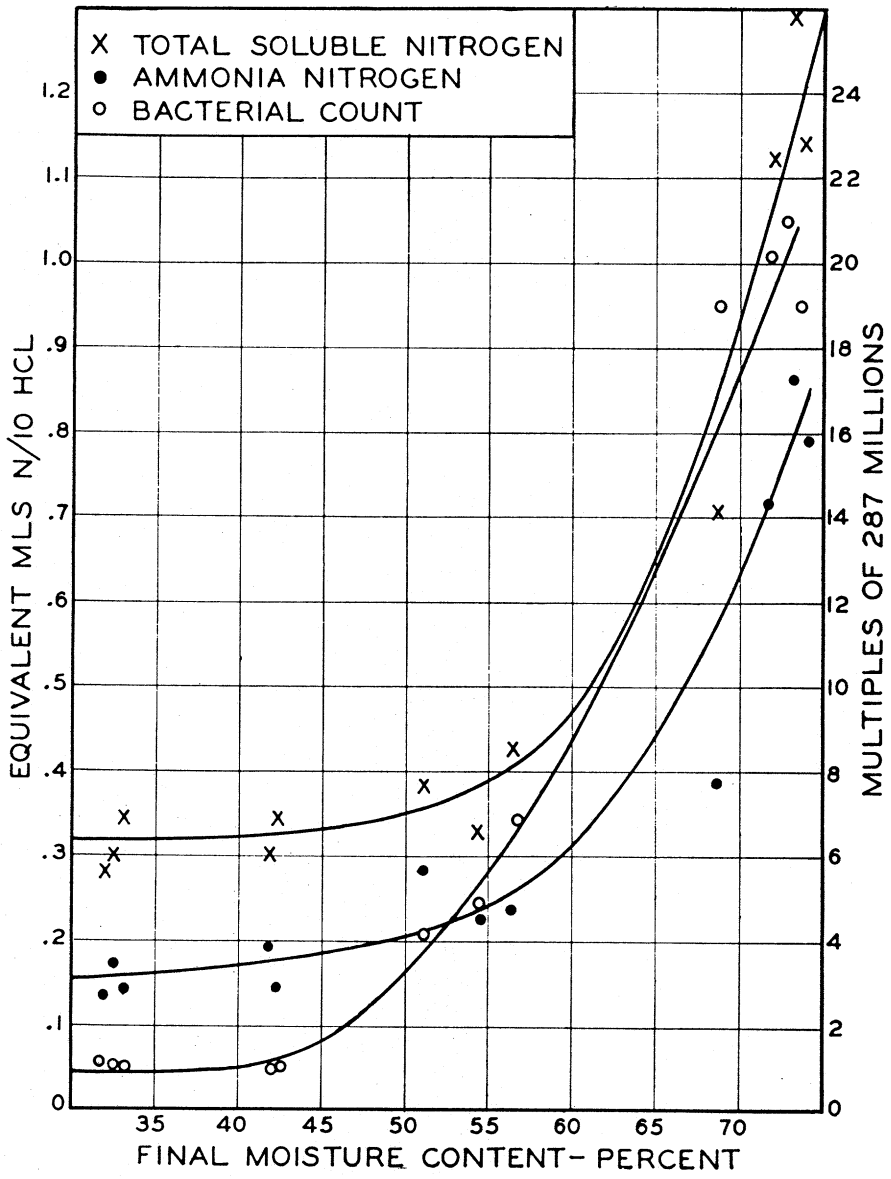

FIGURE III. Total soluble nitrogen, ammonia nitrogen, and bacterial count plotted against final moisture content of cured skin.

content of over 47 per cent. The results given in Table II are presented graphically in Figure II. In this figure a value of 1 has been given to the bacterial count of 287 million since this count was the one obtained per gram of skin cured with salt alone and stored at 88 per cent relative humidity. For simplicity all other counts have been expressed in multiples of this value. Where the count was slightly less than 287 million a value of 1 was also used.

In Figure III the values given in Table II are plotted against the final moisture content of the sample as shown in the last column of Table I. The actual points are indicated and the most probable curves for total soluble nitrogen, ammonia nitrogen, and bacterial count shown with respect to these points. These curves conform closely to those previously published[1] showing the effect of the moisture content on stored salted calfskin. In fact, the close agreement is quite remarkable when one considers that in these experiments the moisture concentration was continually changing during the incubation or storage period.

Discussion and Summary

Previous work has shown that the critical point for the moisture content of salted skins is about 49 to 50 per cent. Moisture in excess of 50 per cent tends to materially accelerate microbial action, whereas, less moisture has a marked retarding or inhibiting effect. The results presented herein are quite in harmony with the foregoing and provide additional confirmation.

The similarity shown between the action of sodium sulfate and sodium carbonate is particularly interesting. The results presented indicate strongly that any inhibiting effect which they may have on the microbial deterioration of salted skins is an indirect one due to their influence in retarding absorption of moisture especially at high relative humidities. No appreciable bacteriostatic activity is shown for either one that could not be accounted for readily on this basis. Apparently marked effects can be obtained by mixing quite small quantities with the salt.

The necessity of carefully considering humidity and moisture in the study of materials proposed for mixing with salt to increase its effectiveness must be emphasized. It is essential that these factors be controlled in small-scale laboratory curing studies, if directly comparable results for the bacteriostatic activity of different chemicals are to be obtained.

References

1. *J. Amer. Leather Chem. Assoc.*, **33**, 198 (1938).
2. *Ibid*, **35**, 554 (1940).
3. *J. Int. Soc. Leather Trades Chem.*, **21**, 55 (1937).
4. *J. Ind. and Eng. Chem.*, **13**, 326 (1921).